



PATENT SPECIFICATION

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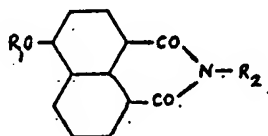
COMPLETE SPECIFICATION

Naphthalimide Optical Whitening Agents

We, MITSUBISHI CHEMICAL INDUSTRIES LIMITED, a joint-stock company organised under the laws of Japan, of 4, 2-chome, Marunouchi, Chiyoda-ku, Tokyo, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 The invention relates to naphthalimide optical-whitening agents, and a method for the manufacture as well as the applications of said optical whitening agents.

15 The invention provides an optical whitening agent comprising a naphthalimide derivative of the following formula (1)

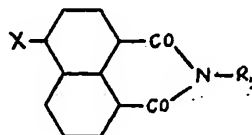


(1)

20 wherein R₁ denotes an alkyl-, an aryl-, or a cycloalkyl-group, which may be substituted; and R₂ denotes a hydrogen atom, an alkyl-, an aryl-, and aralkyl-, or a cycloalkyl-group, which may be substituted R₁ being the same as or different from R₂.

25 The invention includes three different methods of manufacturing the new whitening agents of the invention.

In the first process a compound of the following formula (2):

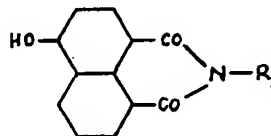


(2)

wherein X denotes a sulpho group, a salt thereof, a nitro group, or a halogen atom, is condensed in the presence of a condensing agent, with a compound of the following formula (3), or a salt thereof:



In the second process a compound of the following formula (4), or a salt thereof:

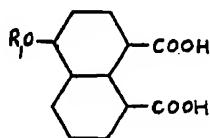


(4)

is etherified with the appropriate etherifying agent.

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In the third process a compound of the following formula (5), or an anhydride thereof:



(5)

5 is condensed with a compound of the following formula (6):

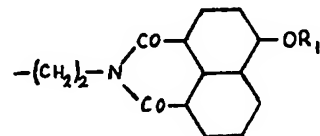


The present invention also includes fixing, permeation, adhesion or mixing of at least one optical whitening agent according to the invention in the course of either the manufacture, the forming or the fabrication of artificial or synthetic organic high molecular weight materials such as textile and plastic materials.

The derivatives of the invention when dissolved or dispersed in a suitable solvent or when applied to a fitting fundamental material emit a distinctive blue-violet fluorescence in daylight or ultraviolet rays showing a side absorption in the ultraviolet range. Further, these compounds generally have good stability and exhibit affinity with artificial or synthetic organic high molecular weight materials. Hence, the derivatives of the invention are able to impart an outstanding and durable optical whitening effect to the above mentioned materials.

The optical whitening agents according to the invention may have as R_1 for example, such alkyl groups of straight chain or branched chain, as methyl, ethyl, *n*- or *iso*-propyl, *n*- or *iso*-butyl, *n*- or *iso*-pentyl, *n*- or *iso*-hexyl, *n*-octyl, 2-ethyl-hexyl, *n*- or *iso*-dodecyl, and *n*- or *iso*-tridecyl. Further, R_1 may be a substituted alkyl group substituted by at least one of hydroxy, alkoxy, primary amino, secondary amino such as alkyl amino, tertiary amino such as bisalkyl amino and quarternary ammonium such as trialkyl ammonium. They may be, for example, hydroxyethyl, hydroxypropyl, hydroxybutyl, methoxyethyl, ethoxyethyl, ethoxypropyl, propoxypropyl aminoethyl, aminopropyl, N,N - dimethyl - amino - ethyl, N,N - dimethylamino - propyl, N - trimethyl ammonium propyl, N-triethyl ammonium ethyl, and N-triethyl ammonium propyl. Still further R_1 may be such aryl group as phenyl and naphthyl or a substituted aryl group substituted by at least one of alkyl, alkoxy, hydroxy, alkoxyalkyl, hydroxyalkyl, amino, secondary aminoalkyl, tertiaryaminoalkyl,

quarternary ammonium alkyl, nitro, and halogen. Still further, R_1 may be such aralkyl group as benzyl or such cycloaliphatic group as cyclohexyl. R_2 may be, for example, such a group as shown by the formula:



60

The three methods of the invention will be described in greater detail in the following:

In the first method the compounds shown by the formula (2) include 4-substituted naphthalimides and their N-substituted compounds which are substituted in the 4-position of naphthalene nucleus by a sulpho group, a salt thereof such as sodium sulphonate ($-SO_3Na$) and potassium sulphonate ($-SO_3K$), nitro group, or halogen atom such as chlorine and bromine. The said N-substituted compounds have organic groups having no dyestuff character as the N-substituents, which have been specified as R_2 in the formula (1). As regards the compounds of the formula (3), on the other hand, there may be cited various organic compounds having no dyestuff character which have an alcoholic hydroxyl group or a phenolic hydroxyl group. Namely, R_1 in the formula (3) includes an organic compound having no dyestuff character which has been explained as R_1 in the formula (1). Among the compounds of the formula (3) there are, for example, such aliphatic alcohols as methanol, ethanol, *n*- or *iso*-propanol, *n*- or *iso*-butanol, *n*- or *iso*-pentanol, *n*- or *iso*-hexanol, 2-ethylhexanol, *n*-octanol, *n*- or *iso*-dodecyl alcohol, and *n*- or *iso*-tridecyl alcohol. These alcohols may in some cases be employed as alcoholate, which is, e.g., sodium alcoholate or potassium alcoholate. The compound of the formula (3) may also be a compound such that the alkyl group in the aforementioned alcohol has been substituted by such a group as hydroxy-, alkoxy, and tertiary amino. Among these there are, for example, ethylene glycol, propylene glycol, butylene glycol, 2-ethoxy-ethanol, 2-ethoxy-propanol, 2-ethoxy - 2 - ethoxy-ethanol, N,N - dimethylamino ethanol, N,N - diethylamino ethanol, N,N - dimethylamino propanol, and N,N-diethylamino propanol. Further, the compound of the formula (3) may be such aralkyl alcohol as benzyl alcohol. Still further, among the compounds of the formula (3) there are such hydroxy aromatic compounds as phenol, phenolates, naphthol, and naphtholates, or a substituted compound thereof substituted in the aromatic nucleus by alkyl, alkoxy,

- hydroxy, nitro, or halogen. The preferred condensing agents are such alkali metal hydroxides as sodium hydroxide and potassium hydroxide. Also such alkali metal salts as carbonates, bicarbonates, phosphates, silicates, and acetates may be employed as condensing agents. Although the condensation reaction is favourably effected when an excess amount of a compound as indicated by formula (3) is used as a diluent, the said reaction may also be performed in a suitable inert solvent. The condensation reaction is performed generally at a temperature in a range from about 30 to 200° C. For example, in the case where such an aliphatic alcohol as methanol, ethanol, ethylene glycol, and propylene glycol as the compound of formula (3) is employed it is advisable to react at the boiling point of the mixture. The reaction product is allowed to precipitate generally at room temperature followed by separation and washing. In some cases the reaction mixture is either acidified or after the diluent or solvent used for the reaction has been distilled off the reaction product is allowed to precipitate followed by separation by way of filtering. The reaction product obtained by such a method is reasonably pure but may be, if required, purified further by washing using alkaline aqueous solution or recrystallization using solvent.
- In the second method among the compounds indicated by the aforementioned formula (4) there are 4-hydroxy-naphthalimides or salts thereof, e.g., sodium salts and potassium salts and their N-substituted compounds. The said N-substituted compounds have an organic group having no dyestuff character as the N-substituents which have been explained as R₂ in formula (1). As regards the etherifying agents to be used for etherifying the compounds as indicated by formula (4), strong acid esters having no dyestuff character may first be mentioned. The representative examples of said strong acid esters are such alkyl sulphates as dimethyl sulphate and diethyl sulphate. As the etherifying agents, may also be cited organic compounds which contain an active halogen atom, the preferred examples of said compounds being alkyl chlorides, alkyl bromides, and alkyl iodides. Also such esters of aryl sulphonic acid as the methyl ester of *p*-toluene sulphonic acid, the ethyl ester of *p*-toluene sulphonic acid may be employed as the etherifying agent. The etherification reaction may be efficiently performed in the presence of such alkaline substances preferably as alkali metal hydroxides, alkali metal carbonates, alkali metal bicarbonates, alkali metal phosphates, alkali metal silicates, and alkali metal acetates. The etherification reaction is effected generally at temperatures in a range from about 30 to 200° C while using preferably suitable diluents or inert solvents. In accordance with such a method the objective product as indicated by formula (1) is obtained.
- In the third method among the compounds as indicated by formula (5) or anhydrides thereof to be applied to this method are 4-substituted naphthalic acids or 4-substituted naphthalic anhydrides with which an organic group R₁ is combined through an oxygen atom in the 4-position of the naphthalene nucleus wherein the aforesaid R₁ signifies various organic groups having no dyestuff character shown as R₁ in formula (1). On the other hand, among the compounds of formula (6) are ammonia or various organic amines having no dyestuff character. They include various alkyl amines such as methyl amine, ethyl amine, *n*- or *iso*-propyl amine, *n*- or *iso*-butyl amine, *n*- or *iso*-hexyl amine, *n*- or *iso*-octyl amine, *n*- or *iso*-dodecyl amine, and *n*- or *iso*-tridecyl amine. In addition, they may be substituted alkyl amines wherein the alkyl group of the foresaid alkyl amines is substituted by such group as hydroxy, alkoxy, primary amino, secondary amino, such as alkyl amino, and tertiary amino such as bis-alkyl amino. Among these substituted alkyl amines are ethanilamine, propanolamine, butanolamine ethylene diamine, propylene diamine, N,N-dimethyl-ethylenediamine, N,N-dimethyl-propylenediamine, methoxyethylamine, ethoxyethylamine, and ethoxypropylamine. As the organic amines indicated by formula (6) such aryl amines as aniline and naphthylamine are also employed. Further, there may be employed substituted aryl amines wherein the aryl group of said amines is substituted by such group as alkyl, alkoxy, hydroxy, alkoxyalkyl, hydroxyalkyl, nitro, amino and halogen. Also such aralkyl amine as benzyl amine and such cycloaliphatic amine as cyclohexylamine may be employed.
- The condensation reaction of a compound of formula (5) with a compound of formula (6) is smoothly effected in the presence of, in general, water, alcohol, a mixture thereof, and such inert diluent as *o*-dichloro-benzene. In some cases the reaction may be performed by employing an excess amount of a compound of formula (6) as the diluent. The condensation reaction efficiently proceeds at a suitable temperature in a range of 10 to 200° C. Such treatment yields the objective product as indicated by formula (1).
- The individual optical whitening agents as indicated by formula (1) exert remarkable whitening effect on various materials, particularly on artificial or synthetic organic high molecular weight materials by fixing, penetrating, mingling, or adhering.
- The treatment of such polyester textile material as polyethylene terephthalate is generally performed in accordance with conventional methods for dyeing this textile material by using an aqueous dispersing

medium containing the optical whitening agent of the invention. For this purpose, a treating bath is made up by way of uniformly dispersing the optical whitening agents in water by use of a suitable dispersing agent and/or wetting agent, said bath being used for dipping or padding polyester textile material at a temperature up to 100° C. In some cases, the so-called carrier dyeing method may be carried out wherein such "carrier" as chlorobenzene is employed. Also so-called high temperature dyeing or thermosol process to be employed for dyeing polyester textile material is applicable as the method of treatment according to the invention. Polyester textile material thus treated emits blue violet fluorescence in daylight or ultraviolet rays. Hence, a remarkable whitening effect is imparted while neutralizing the yellowish tint of textile material. The optical whitening agents according to the invention may be efficiently applied to various types of synthetic or artificial textile materials including such polyvinyl textile materials as polyacrylonitrile and polyvinylchloride; such nitrogen-containing textile material as polyamide; such polyolefin textile material as polypropylene; and such cellulose ester as cellulose acetate. The optical whitening agents according to the invention are also applicable to whiten such moulded materials as film, sheet, plate, board, tube, pipe, and block, which are made of various synthetic or artificial resins. For example, mixing the optical whitening agent according to the invention with such synthetic resin as polystyrene followed by such moulding as extrusion and injection results in producing a transparent moulded material, which emits blue-violet fluorescence. The optical whitening agents according to the invention are also applied to the white-enhancing treatment of various moulded materials composed of synthetic resins such as polyvinyl chloride, polyacrylate, polyester, polycarbonate, polyurethane, polyamide, and polyolefin. As a result of these treatments an excellent white-enhancing effect is always bestowed although the degree is not exactly the same.

The white-enhancing treatments by use of the optical whitening agents according to the invention may be carried out by methods other than the above mentioned methods. For example, mixing of the optical whitening agents according to the invention may be carried out in a suitable step during the process of manufacturing textile material or synthetic resin. Further, it may be feasible to spread on the surfaces of the material a suitable solvent in which the optical whitening agents is contained.

Some preferred embodiments of the invention will be described in detail in the following Examples given for the purpose of illustrating the invention. The "part" in the

following denotes the portion by weight unless otherwise specified. The melting point of the compounds shown in the following Examples is the uncorrected value.

EXAMPLE 1.

30 parts of sodium hydroxide are dissolved in 300 parts of methanol. To the solution are added 30 parts of sodium salt of N-methylnaphthalimide-4-sulphonic acid and heated while stirring for 10 hr. under reflux. Upon completion of the reaction the solution is allowed to cool. Then precipitate is separated by filtering which is washed with methanol and then warm water and dried. Thus obtained were 22.8 parts of N-methyl-4-methoxy-naphthalimide having melting point of 198.8—199.2° C. This product emits remarkable blue-violet fluorescence in such solvents as methanol and glacial acetic acid. The analytical values of this product closely approximate to the calculated values as follows:

	C(%)	H(%)	N(%)
Calcd. for $C_{14}H_{11}NO_3$	69.70	4.59	5.80
Found	69.61	4.84	5.73

EXAMPLE 2.

30 parts of sodium hydroxide are dissolved in 300 parts of methanol followed by the addition of 30 parts of N-methyl-4-bromonaphthalimide and the heating while stirring for 10 hr. under reflux. Upon completion of the reaction, the reaction mixture is subjected to the same treatment as in Example 1 to obtain 24 parts of N-methyl-4-methoxynaphthalimide of the same grade to that in Example 1. The same result was obtained in the case where N-methyl-4-chloronaphthalimide was used in place of starting material N-methyl-4-bromo-naphthalimide.

EXAMPLE 3.

30 parts of sodium hydroxide are dissolved in 300 parts of methanol to which 30 parts of N-methyl-4-nitro-naphthalimide are added and heated while stirring for 10 hr. under reflux. Upon completion of the reaction the same treatments have been conducted as in Example 1 to obtain 24 parts of N-methyl-4-methoxy-naphthalimide of the same grade to that in Example 1.

EXAMPLE 4.

21.1 parts of sodium hydroxide and 50.0 parts of N-methyl-4-hydroxy-naphthalimide are dissolved in 500 parts of water. To the

aqueous solution are added by degrees 55.5 parts of dimethyl sulphate followed by stirring at 30° C. for 1 hr. to subsequently conduct the reaction for 1 hr. at 60° C. Upon completion of the reaction, the reaction mixture is allowed to cool and then subjected to filtration for separating precipitate, which is washed in sequence by an aqueous dilute solution of sodium carbonate and water and dried to obtain 15 parts of N-methyl-4-methoxynaphthalimide of the same grade as in Example 1. The same results are brought about by the use of potassium hydroxide or potassium carbonate in place of the aforesaid sodium hydroxide.

EXAMPLE 5.

42.0 parts of sodium carbonate and 50.0 parts of N-methyl-4-hydroxy-naphthalimide are dissolved in 500 parts of water. To the aqueous solution are added by degrees 83.2 parts of dimethyl sulphate and stirred for 1 hr. at 60° C and subsequently reacted at 95° C for 15 min. Upon completion of the reaction, the same treatment is conducted as in Example 1 to obtain 30.0 parts of 4-methoxynaphthalimide of the same grade as in Example 1.

EXAMPLE 6.

33.3 parts of dimethyl sulphate are added by degrees while stirring to a mixture comprising 300 parts of methanol, 16.7 parts of sodium carbonate, and 30.0 parts of N-methyl-4-hydroxy-naphthalimide and heated under reflux to perform a reaction for 2 hr. Upon completion of the reaction, methanol is distilled off, then water is added to the residue and filtered to separate the precipitate, which is separated by way of filtration. The subsequent procedure is conducted similarly as in Example 4 to obtain 9.0 parts of N-methyl-4-methoxy-naphthalimide of the same grade as in Example 1.

EXAMPLE 7.

1.3 parts of sodium carbonate, 5.0 parts of N-methyl-4-hydroxy-naphthalimide, and 4.5 parts of methyl ester of *p*-toluene sulphonic acid are added to 50 parts of *o*-dichlorobenzene followed by heating to perform a reaction for 5 hr. at 170° C, i.e., the boiling point. Upon completion of the reaction, *o*-dichlorobenzene is distilled off by way of steam distillation then the residue is filtered to separate precipitate. The precipitate is subjected to the same treatment as in Example 4 to obtain 4.6 parts of N-methyl-4-methoxynaphthalimide as in Example 1.

EXAMPLE 8.

10.0 parts of 4-methoxy-naphthalimide anhydride are added to 136 parts of 10% methylamine aqueous solution and allowed to react overnight at room temperatures under

stirring. Then the precipitate is separated by filtering followed by washing and drying to obtain 10.0 parts of N-methyl-4-methoxynaphthalimide of the same grade as in Example 1.

EXAMPLE 9.

A mixture comprising 114 parts of phenol and 15 parts of potassium hydroxide is heated at 140° C to remove the moisture and allowed to cool. To the resultant mixture are added 50 parts of N-methyl-4-bromo-naphthalimide and heated at 140° C to perform a reaction for 7 hr. The reaction mixture is discharged into a dilute aqueous solution of sodium hydroxide to segregate precipitate, which is taken out by way of filtration followed by washing and drying to obtain 52 parts of crude N-methyl-4-phenoxy-naphthalimide. The recrystallisation of this product by use of acetic acid yields a pure substance having melting point of 177.5—178.5° C. The analytical values of this substance emitting a remarkable blue-violet fluorescence in solvents closely approximate to the calculated values as shown in the following table

	C(%)	H(%)	N(%)
Calcd. for $C_{19}H_{13}NO_3$	75.24	4.32	4.62
Found	74.55	4.39	4.48

EXAMPLE 10.

A mixture comprising 123 parts of phenol and 35 parts of potassium hydroxide is dehydrated at 140° C and allowed to cool. To the resultant mixture are then added 50 parts of N-methyl-4-nitro-naphthalimide which is again heated at 95—100° C for 7 hr. The reaction mixture is subjected to the same treatment as in Example 9 to obtain 58 parts of N-methyl-4-phenoxy-naphthalimide of the same grade as in Example 9.

EXAMPLE 11.

20 parts of sodium hydroxide are dissolved in 200 parts of methanol. To the solution are added 20 parts of sodium salt of N-phenylnaphthalimide-4-sulphonic acid and heated under reflux for 20 hr. Upon completion of the reaction, 200 parts of water are added to the reaction mixture followed by filtration to take out the precipitate, which is washed and dried. Thus obtained are 10 parts of N-phenyl-4-methoxy-naphthalimide having a melting point of 244.3—244.8° C. This substance emits remarkable blue-violet fluorescence in solvents. The analytical values of the substance closely approximate to the calculated values as follows:

	C(%)	H(%)	N(%)
Calcd. $C_{18}H_{13}NO_3$	75.24	4.32	4.62
Found	74.31	4.44	4.58

EXAMPLE 12.

30.0 parts of sodium salt of N-methylnaphthalimide-4-sulphonic acid are added to a solution comprising 300 parts of 2-ethoxyethanol and 30.0 parts of sodium hydroxide followed by heating at 80° C for 1 hr. Upon completion of the reaction, the reaction mixture is allowed to cool. The precipitate is taken out by filtration which is washed and dried to obtain 16.2 parts of N-methyl-4-(2'-ethoxy)-ethoxy-naphthalimide having melting point of 124.5—126.0° C. This substance emits blue-violet fluorescence in solvents and the analytical values closely approximate to the calculated values as follows:

	C(%)	H(%)	N(%)
Calcd. for $C_{17}H_{17}NO_4$	68.21	5.73	4.68
Found	67.59	5.65	4.52

EXAMPLE 13.

50.0 parts of sodium salt of N-methylnaphthalimide-4-sulphonic acid are added to a solution comprising 500 parts of benzyl alcohol and 25.0 parts of sodium hydroxide and heated at 75—85° C. for 10 hr. Upon completion of the reaction, the reaction mixture is allowed to cool and then 500 parts of methanol are added followed by filtration to take out the precipitate, which is washed by methanol and subsequently by water and dried. Thus, 37 parts of N-methyl-4-benzoyloxy-naphthalimide having melting point of 198.8—200.5° C are obtained. This substance emits remarkable fluorescence in solvents and the analytical values closely approximate to the calculated values as shown in the following

	C(%)	H(%)	N(%)
Calcd. for $C_{20}H_{15}NO_3$	75.69	4.76	4.41
Found	75.24	4.99	4.39

EXAMPLE 14.

A mixture comprising 123 parts of phenol and 35 parts of potassium hydroxide is dehydrated at 140° C, and then allowed to cool. 30 parts of N-phenyl-4-nitro-naphthalimide are added to the resultant mixture followed by heating at 120° C for 12 hr. Upon completion of the reaction, the reaction mixture is discharged into a dilute aqueous solution of sodium hydroxide. The precipitate is taken out by filtering which is washed and dried. Thus 28 parts of crude N-phenyl-4-phenoxy-naphthalimide having melting point of 271.2—273.8° C are obtained. Recrystallisation of this substance by use of acetic acid yields a refined product having melting point of 274.0—275.2° C. The analytical values are as follows:

	C(%)	H(%)	N(%)
Calcd. for $C_{24}H_{15}NO_3$	78.89	4.14	3.83
Found	78.74	4.09	3.88

EXAMPLE 15.

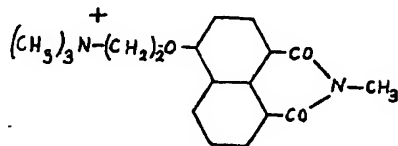
31 parts of sodium salt of N-methylnaphthalimide-4-sulphonic acid are added to a mixture comprising 300 parts of dioxane (solvent), 6.8 parts of ethylene glycol, and 3 parts of sodium hydroxide and allowed to perform a reaction under reflux for 5 hr. Upon completion of the reaction, the reaction mixture is allowed to cool. The precipitate is removed by filtering, washed and dried to obtain 10 parts of N-methyl-4-(2'-hydroxy)-ethoxy-naphthalimide having melting point of 196.8—198.5° C. The analytical values are as follows:

	C(%)	H(%)	N(%)
Calcd. for $C_{15}H_{13}NO_4$	66.41	4.83	5.16
Found	65.69	4.87	5.15

EXAMPLE 16.

30.0 parts of sodium salt of N-methylnaphthalimide-4-sulphonic acid are added to a mixture comprising 300 parts of N,N-dimethylaminoethanol and 30.0 parts of sodium hydroxide followed by heating at 70° C for 3 hr. Upon completion of the reaction, the reaction mixture is allowed to cool. The precipitate is removed by filtering, washed and dried. Thus 21.9 parts of N-methyl-4-N¹.N¹-dimethylamino-ethoxy-naphthalimide are

- obtained which has melting point of 142.8—144.0° C. In case this substance is dissolved in toluene (solvent) followed by the addition of methylating agent either dimethyl sulphate or methyl ester of *p*-toluene sulphonic acid at a temperature from 30 to 60° C there is produced a compound of the formula as follows:



EXAMPLE 17.

- 33.6 parts of sodium carbonate and 30.0 parts of N-methyl-4-hydroxy-naphthalimide are dissolved in 300 parts of water. To the solution are added by degrees 81.4 parts of diethyl sulphate and stirred at 60° C for 2 hr. followed by reaction at 95° C for 15 min. The reaction mixture is allowed to cool, and then the precipitate is taken out, washed and dried. Thus, 15.0 parts of N-methyl-4-ethoxy-naphthalimide having melting point of 167.5—168° C are obtained. The analytical values of this substance closely approximate to the calculated values as follows:

	C(%)	H(%)	N(%)
Calcd. for $\text{C}_{15}\text{H}_{13}\text{NO}_3$	70.58	5.13	5.49
Found	70.01	5.20	5.36

EXAMPLE 18.

- 56.2 parts of ethyl iodide are added to a solution comprising 300 parts of water, 16.1 parts of sodium carbonate, and 30.0 parts of N-methyl-4-hydroxy-naphthalimide followed by a reaction under reflux for 3 hr. Upon completion of the reaction, the reaction mixture is subjected to the same treatment as in Example 17 to obtain 4.0 parts of N-

methyl-4-ethoxy-naphthalimide which is the same as in Example 17.

EXAMPLE 19.

21.3 parts of ethylene chlorohydrin are added to a solution comprising 300 parts of water, 11.6 parts of sodium carbonate, and 30.0 parts of N-methyl-4-hydroxy-naphthalimide and heated at 60° C for 2 hr. followed by reaction at 95° C for 30 min. The reaction mixture is acidified by adding hydrochloric acid and the precipitate is removed by filtering. The precipitate is subjected to refining by use of acetic acid to obtain 31.0 parts of the same N-methyl-4-(2'-hydroxy)-ethoxy-naphthalimide as in Example 15.

EXAMPLE 20.

10.0 parts of 4-methoxy-naphthalic anhydride are added to 100 parts of aniline to perform a reaction under reflux for 1 hr. Upon completion of the reaction, the reaction mixture is subjected to steam distillation to distil off excess of aniline. The precipitate is washed in sequence by dilute hydrochloric acid and water and dried to obtain 13.0 parts of the same N-phenyl-4-methoxy-naphthalimide as in Example 11.

EXAMPLE 21.

10.0 parts of 4-methoxy-naphthalic acid are added to 140 parts of 10% ammonia aqueous solution and heated at 90° for 1 hr. Upon completion of the reaction, the precipitate is taken out by filtration which is then washed and dried to obtain 10.0 parts of 4-methoxy-naphthalimide having melting point of 307.5—309° C. This substance has analytical values as follows:

	C(%)	H(%)	N(%)
Calcd. for $\text{C}_{13}\text{H}_9\text{NO}_3$	68.72	3.99	6.17
Found	67.57	4.33	6.20

EXAMPLES 22 TO 29.
A compound shown in the following columns
A and B is respectively caused to perform a

reaction by the method as described in Ex-
ample 1 to obtain the novel optical whitening
agent correspondingly indicated in column C.

5

A	B	C
Ex. 22 ethanol	sodium salt of N-methyl-naphthalimide-4-sulphonic acid	N-methyl-4-ethoxy-naphthalimide
Ex. 23 <i>n</i> -butanol	ditto	N-methyl-4-butoxy-naphthalimide
Ex. 24 2-ethyl-hexanol	sodium salt of N-methyl-naphthalimide-4-sulphonic acid	N-methyl-4-(2 ¹ -ethyl)-hexyloxy-naphthalimide
Ex. 25 methanol	sodium salt of N-butyl-naphthalimide-4-sulphonic acid	N-butyl-4-methoxy-naphthalimide
Ex. 26 ditto	sodium salt of N-(2 ¹ -hydroxy)-ethyl-naphthalimide-4-sulphonic acid	N-(2 ¹ -hydroxy)-ethyl-4-methoxy-naphthalimide
Ex. 27 ditto	sodium salt of N-benzyl-naphthalimide-4-sulphonic acid	N-benzyl-4-methoxy-naphthalimide
Ex. 28 ditto	sodium salt of N-cyclohexyl-naphthalimide-4-sulphonic acid	N-cyclohexyl-4-methoxy-naphthalimide
Ex. 29 ditto	sodium salt of N-(N ¹ .N ¹ -dimethylamino)-propyl-4-sulphonic acid	N-(N ¹ .N ¹ -dimethylamino)-propyl-4-methoxy-naphthalimide

EXAMPLES 30 TO 37.
A compound shown in the following columns
A and B is respectively caused to perform a

reaction by the method as described in Ex-
ample 9 to obtain the novel optical whitening
agent correspondingly indicated in column C.

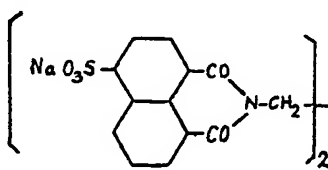
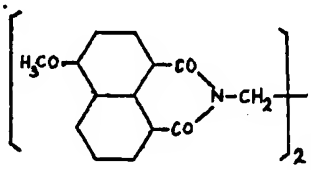
10

A	B	C
Ex. 30 phenol	N-butyl-4-chloro-naphthalimide	N-butyl-4-phenoxy-naphthalimide
Ex. 31 ditto	N-(2 ¹ -ethyl)-hexyl-4-chloro-naphthalimide	N-(2 ¹ -ethyl)-hexyl-4-phenoxy-naphthalimide
Ex. 32 ditto	N-(2 ¹ -hydroxy)-ethyl-4-chloro-naphthalimide	N-(2 ¹ -hydroxy)-ethyl-4-phenoxy-naphthalimide
Ex. 33 ditto	N-(N ¹ .N ¹ -dimethylamino)-propyl-4-chloro-naphthalimide	N-(N ¹ .N ¹ -dimethylamino)-propyl-4-phenoxy-naphthalimide
Ex. 34 ditto	N-benzyl-4-chloro-naphthalimide	N-benzyl-4-phenoxy-naphthalimide
Ex. 35 <i>p</i> -chloro-phenol	N-methyl-4-chloro-naphthalimide	N-methyl-4-(4 ¹ -chloro)-phenoxy-naphthalimide
Ex. 36 <i>p</i> -cresol	N-methyl-4-chloronaphthalimide	N-methyl-4-(4 ¹ -methyl)-phenoxy-naphthalimide
Ex. 37 2-naphthol	ditto	N-methyl-4-(2 ¹ -naphthyl)-oxy-naphthalimide

EXAMPLES 38 TO 45.

A compound shown in the following columns
A and B is respectively caused to perform a

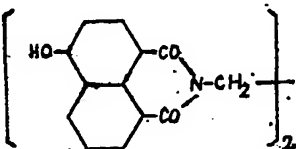
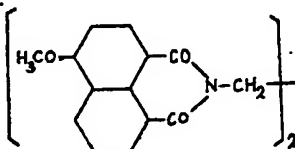
reaction by the method described in Example
11 to obtain the novel optical whitening
agent indicated correspondingly in column C.

	A	B	C
Ex. 38	methanol	sodium salt of N-(4 ¹ -diethyl-amino)-phenyl-naphthalimide-4-sulphonic acid	N-(4 ¹ -diethylamino)-phenyl-4-methoxy-naphthalimide
Ex. 39	ditto	sodium salt of N-(2 ¹ -ethyl)-hexyl-naphthalimide-4-sulphonic acid	N-(2 ¹ -ethyl)-hexyl-4-methoxy-naphthalimide
Ex. 40	ditto		
Ex. 41	ditto	sodium salt of naphthalimide-4-sulphonic acid	4-methoxy-naphthalimide
Ex. 42	ditto	sodium salt of N-(4 ¹ -methyl)-phenyl-naphthalimide-4-sulphonic acid	N-(4 ¹ -methyl)-phenyl-4-methoxy-naphthalimide
Ex. 43	ditto	sodium salt of N-(4 ¹ -methoxy)-phenyl-naphthalimide-4-sulphonic acid	N-(4 ¹ -methoxy)-phenyl-4-methoxy-naphthalimide
Ex. 44	ditto	sodium salt of N-(4 ¹ -chloro)-phenyl-naphthalimide-4-sulphonic acid	N-(4 ¹ -chloro)-phenyl-4-methoxy-naphthalimide
Ex. 45	ditto	sodium salt of N-naphthyl-naphthalimide	N-naphthyl-4-methoxy-naphthalimide

EXAMPLES 46 TO 52.
A compound shown in columns A and B is
caused to perform reaction by the method of

Example 17 or Example 18 to obtain the
novel optical whitening agent indicated corre-
spondingly in column C.

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	A	B	C
Ex. 46	dimethyl sulphate	4-hydroxy-naphthalimide	4-methoxy-naphthalimide
Ex. 47	ditto	N-butyl-4-hydroxy-naphthalimide	N-butyl-4-methoxy-naphthalimide
Ex. 48	ditto	N-(2'-hydroxy)-ethyl-4-hydroxy-naphthalimide	N-(2'-hydroxy)-ethyl-4-methoxy-naphthalimide
Ex. 49	ditto	N-benzyl-4-hydroxy-naphthalimide	N-benzyl-4-methoxy-naphthalimide
Ex. 50	ditto	N-cyclohexyl-4-hydroxy-naphthalimide	N-cyclohexyl-4-methoxy-naphthalimide
Ex. 51	ditto		
Ex. 52	n-butyl-bromide	N-methyl-4-hydroxy-naphthalimide	N-methyl-4-butoxy-naphthalimide

EXAMPLES 53 TO 62.

A compound shown in columns A and B is respectively caused to perform reaction by the

method of Example 8 to obtain the novel optical whitening agent indicated correspondingly in column C. 5

	A	B	C
Ex. 53	4-methoxy-naphthalic acid	n-butylamino	N-butyl-4-methoxy-naphthalimide
Ex. 54	ditto	2-ethyl-hexylamine	N-(2 ¹ -ethyl)-hexyl-4-methoxy-naphthalimide
Ex. 55	ditto	2-hydroxy-ethylamine	N-(2 ¹ -hydroxy)-ethyl-4-methoxy-naphthalimide
Ex. 56	ditto	benzylamine	N-benzyl-4-methoxy-naphthalimide
Ex. 57	ditto	cyclohexylamine	N-cyclohexyl-4-methoxy-naphthalimide
Ex. 58	4-ethoxy-naphthalic acid	methylamine	N-methyl-4-ethoxy-naphthalimide
Ex. 59	4-butoxy-naphthalic acid	ditto	N-methyl-4-butoxy-naphthalimide
Ex. 60	4-(2 ¹ -ethoxy)-ethoxy-naphthalic acid	methylamine	N-methyl-4-(2 ¹ -ethoxy)-ethoxy-naphthalimide
Ex. 61	4-benzyloxy-naphthalic acid	ditto	N-methyl-4-benzyloxy-naphthalimide
Ex. 62	4-phenoxy-naphthalic acid	ditto	N-methyl-4-phenoxy-naphthalimide

EXAMPLE 63.

10 1 part of N-methyl-4-methoxy-naphthalimide is mixed with 2 parts of dispersing agent such as a condensate of naphthalene-2-sulphonic acid with formaldehyde. The mixture is pulverized into easily dispersible powder. The powder is dispersed in 6,000 15 parts of water to prepare a treatment bath. 30 parts of carrier (chlorobenzenes) are added to the bath in which 200 parts of polyester textile material are treated at a temperature from 98 to 100° C for 2 hr. The treated 20 textile material is subjected to soaping in 2,000 parts of aqueous solution containing 6 parts of anion surface active agent at 90° C for 15 min. and then rinsed and dried. Thus 25 the polyester textile material has been imparted a remarkable whitening effect with a good fastness. The same results as in this Example were obtained in the case where the compounds obtained by the methods in Examples 9 to 62 were used.

EXAMPLE 64.

30 1 part of N-butyl-4-methoxy-naphthalimide is mixed with 2 parts of dispersing agent constituting a condensate, which consists of 2-naphthol-6-sulphonic acid, cresol and formaldehyde. The mixture is pulverized into 35 easily dispersible powder. The powder is dispersed in 6,000 parts of water to prepare a treatment bath. In this bath are immersed 200 parts of polyester textile material to be subjected to a treatment at 120° C for 1.5 40 hr. The treated textile material is then subjected in sequence to soaping, rinsing and drying as in Example 63. Thus remarkably whitened polyester textile material is obtained. Any of various compounds in Examples 1 to 45 62 may be used for performing the same treatment as in the present Example to obtain similarly whitened polyester textile material as in this Example.

EXAMPLE 65.

1 part of N-methyl-4-methoxy-naphthalimide is dispersed in 6,000 parts of water to prepare a treatment bath as in Example 64. In the bath are immersed 200 parts of cellulose acetate textile material and heated at 85° C for 1 hr. Then, thus treated textile material is subjected to soaping at 50° C, rinsing and drying. Thus, the treated textile material has been imparted a remarkable whitening effect.

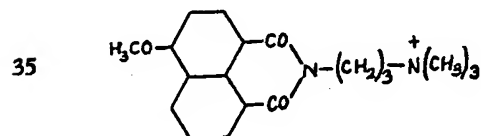
200 parts of polyamide textile material or polyacrylonitrile textile material in place of cellulose acetate material may be subjected to the same treatment at 100° C as in this Example to impart to the respective textile material a remarkable whitening effect. Further, the whitening of these textile materials is effected also in the case where any of compounds in Examples 9 to 62 is used.

EXAMPLE 66.

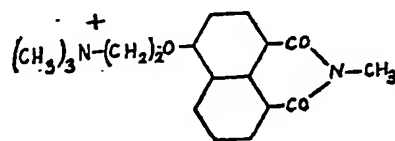
A mixture of 2 parts of N-methyl-4-methoxy-naphthalimide and 2 parts of dispersing agent is dispersed in 15,000 parts of water to prepare a treatment bath as in Example 64. In the bath are immersed 500 parts of polypropylene textile material followed by heating at 98 to 100° C for 1 hr. and then soaping, rinsing, and drying. Thus a remarkable whitening is imparted to polypropylene textile material.

EXAMPLE 67.

2 parts of compound as indicated by the following formula:



are dissolved in 3,000 parts of aqueous solution containing 0.5 parts of acetic acid and 1.0 part of sodium acetate to prepare a treatment bath in which 100 parts of polyacrylonitrile textile material are immersed and heated at about 100° C for 1.5 hr. followed by soaping, rinsing, and drying. Thus a remarkable whitening is imparted to polyacrylonitrile textile material. Similar whitening is also effected in the case where the compound as indicated in the following formula is used:



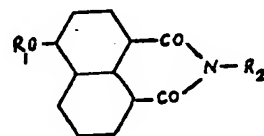
EXAMPLE 68.

A mixture of 2 parts of N-phenyl-4-methoxy-naphthalimide and 1,000 parts of polystyrene resin pellet is kneaded at 200—240° C, and then moulded in plate at 220—260° C by using an injector. Thus a transparent plate is obtained which emits outstanding blue-violet fluorescence.

By adding 20 to 50 parts of titanium dioxide in the course of the aforementioned kneading a white-enhanced plate is obtained. Similar effect is brought about in the case where any compound in Examples 1 to 62 is used. Further, similar white-enhancing is also imparted to polyvinylchloride resin, polyacrylate resin, polyamide resin, polyester resin, and polycarbonate resin as used in place of polystyrene resin in this Example.

WHAT WE CLAIM IS:—

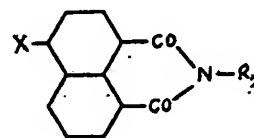
1. An optical whitening agent comprising a naphthalimide derivative of the following formula (1);



(1)

wherein R₁ denotes an alkyl-, an aryl-, or a cycloalkyl-group, which may be substituted; and R₂ denotes a hydrogen atom, an alkyl-, an aryl-, an aralkyl-, or a cycloalkyl-group which may be substituted, R₁ being the same as or different from R₂.

2. A method of manufacturing a naphthalimide derivative as claimed in Claim 1 in which a compound of the following formula: (2)



(2)

wherein X denotes a sulpho group, a salt thereof, a nitro group, or a halogen atom, is condensed in the presence of a condensing agent with a compound of the following formula: (3) or a salt thereof



3. A method of manufacturing a naphthalimide derivative as claimed in Claim 1 in which a compound of the following formula (4), or a salt thereof

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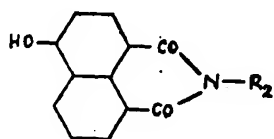
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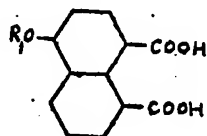
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(4)

is etherified with the appropriate etherifying agent.

- 5 4. A method of manufacturing a naphthalimide derivative as claimed in Claim 1 in which a compound of the following formula (5), or an anhydride thereof:



(5)

is condensed with a compound of the following formula (6):

10



5. A method of optical whitening an artificial or synthetic organic high molecular weight material which comprises treating the said material with a naphthalimide derivative as claimed in Claim 1.

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6. A method as claimed in Claim 5 which comprises treating an artificial or synthetic textile material with the naphthalimide derivative in an aqueous medium.

20

7. A method as claimed in Claim 5 which comprises mingling an artificial or synthetic plastic material with the naphthalimide derivative.

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